AI-70-22

FINAL REPORT
FOR
ALUMINUM BONDED LEAD TELLURIDE THERMOELECTRIC MODULE STUDY FOR NON-MAGNETIC AND VACUUM APPLICATIONS

(5 March 1968 – 5 February 1970)

Contract No. NAS 5-11514

Prepared by
Atomics International
A Division of North American Rockwell Corporation
Post Office Box 309
Canoga Park, California 91304
for
Goddard Space Flight Center
Greenbelt, Maryland

NOTICES

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SUMMARY

This report covers the 23 month period, March 5, 1968 to February 5, 1970, but it details particularly the progress made since November 5, 1968, the closing date of the prior Summary Report, AI-69-16. The general analysis of test results includes the whole contract period, as well as the period of the predecessor contract NAS 5-10184, and certain closely relevant data from other programs.

The principal items of recent progress are: demonstration that a tungsten barrier between the "P" hot junction and the aluminum hot strap greatly retards degradation; and corroborative evidence that close-fitting of the thermal insulation is necessary to and will inhibit serious sublimation of PbTe at the higher operating temperatures.

The conclusions derived from the total program experience of 45 months are as follows:

The aluminum - contacting technique for PbTe can be applied to practical thermoelectric converters incorporating only materials of very low magnetic permeability.

Good technical performance, mechanical integrity, circuit reliability, and operability in space vacuum are all confirmed by test.

The operational stability is such as to give good end-of-life conversion efficiencies for long missions, e.g., 4% at 15 years.

I. INTRODUCTION

A prior contract, NAS5-10184, was begun in May 1966 and completed approximately 14 months later, in July 1967. The purpose had been to investigate the basic characteristics of the AI proprietary bonded aluminum contact used with 3M Co. PbTe types TEGS-2N, -3N, and -2P; and to place on operational test several 3-couple modules in order to make practical measurements of electrical characteristics and obtain information on operational stability. All aspects were so favorable that it was proposed to continue the small-module tests that were in operation, and to add certain technical tasks of special interest. Reports of this initial program are identified as AI-66-158, AI-66-260, AI-67-99 and AI-67-132.

During the period August 1967 to March 1968, Atomics International continued the operational testing of six 3-couple modules, in order that the accumulation of operational time would not be interrupted. In March 1968, the program reported herein was initiated; it turned out to be an 8-month program with a 15-month extension, thus running 23 months to February 1970. Altogether, the technical effort of the two programs extended over a period of nearly four years.

A very complete "Summary" report was issued for the 8-month period 5 March 1968 to 5 November 1968, identified as AI-69-16. Because the latter 15 months has involved no development, construction, nor destructive examinations, but only continued operational testing of seven thermoelectric modules, the present discussion will be based on, and limited to extension of that summary report.

II. DISCUSSION

A. OPERATIONAL TEST RESULTS, SUMMARIZED

1. SMT-1

This 3-couple module was operated a total of 26,500 hours at average $T_H = 720^oF \pm 10^oF$ and maximum $T_H = 750^oF \pm 10^oF$. The total operational degradation was 18.2%. See Figure 1.

2. SMT-2

This 3-couple module was operated a total of 25,500 hours at average $T_H = 670^oF \pm 10^oF$ and maximum $T_H = 700^oF \pm 10^oF$. The total operational degradation was 9.83%. See Figure 2.

3. SMT-3, -4, -5, -6

Replaced early in program -- see Summary Report, AI-69-16.

4. SMT-7 and SMT-8

These two 3-couple modules were operatedtogether in a common test station for a total period of 14,400 hours, at average $T_H = 740^oF \pm 10^oF$ and maximum $T_H = 750^oF \pm 10^oF$. The total operational degradation was 18.7%. See Figure 3.

5. SMT-9 and SMT-10

These two 3-couple modules were operated together in a common test station for a total period of 10,100 hours, at average $T_H = 780^oF \pm 10^oF$ and maximum $T_H = 800^oF \pm 10^oF$. At 6000 hours, the total operational degradation was 4.1%. At this time, SMT-9 began catastrophic failure; at 7000 hours, SMT-10 did likewise. See Figure 4.

6. LMT-1

This 24 couple module was operated for a total period of 12,350 hours at average $T_H = 700^oF \pm 10^oF$ and maximum $T_H = 725^oF \pm 10^oF$. The total operational power degradation was 9.19%. The "raw" efficiency (electrical power out/electrical heat in) degraded from 3.71% to 3.37% (9.16% change). See Figure 5.

A more detailed review of the test results is given in the following sections II.B. and II.C.

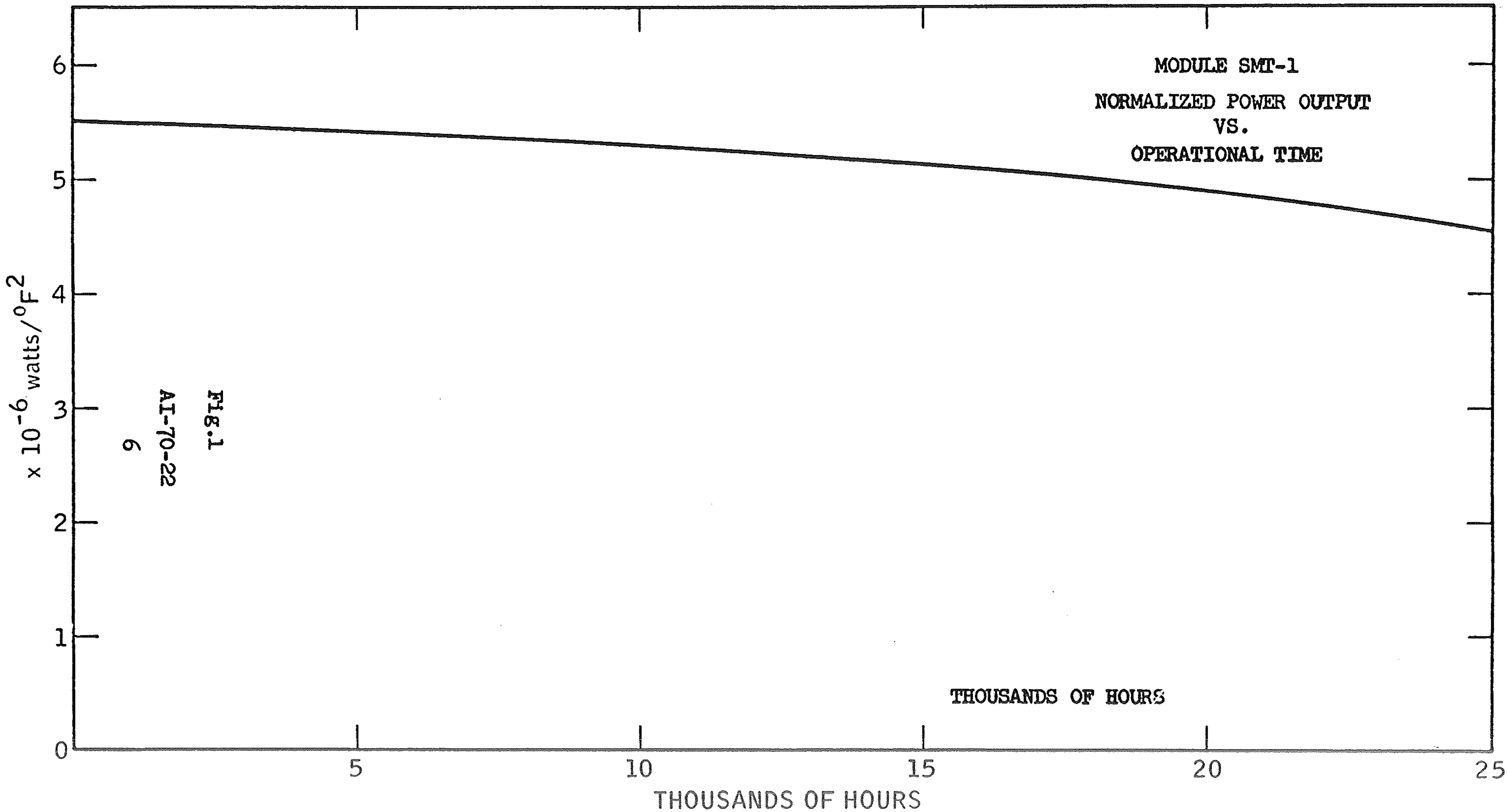
MODULE SMT-1
NORMALIZED POWER OUTPUT
VS.
OPERATIONAL TIME
THOUSANDS OF HOURS
x 10^-6 watts/°F^2
0
1
2
3
4
5
6
5
10
15
20
25
THOUSANDS OF HOURS

Fig.1

AI-70-22

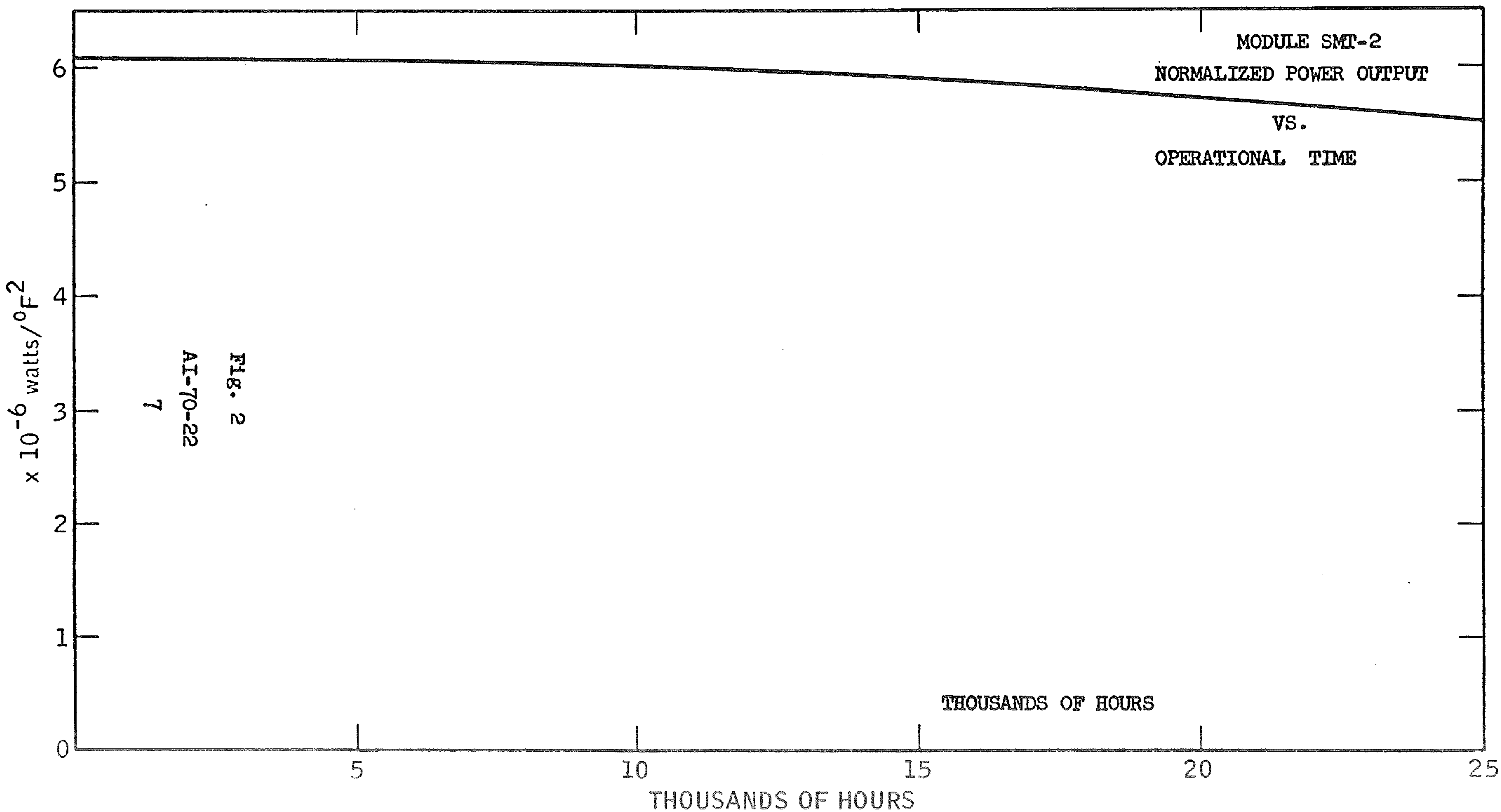
MODULE SMT-2
NORMALIZED POWER OUTPUT
VS.
OPERATIONAL TIME
THOUSANDS OF HOURS
x 10^-6 watts/°F^2
0
1
2
3
4
5
6
5
10
15
20
25
THOUSANDS OF HOURS

Fig. 2

AI-70-22

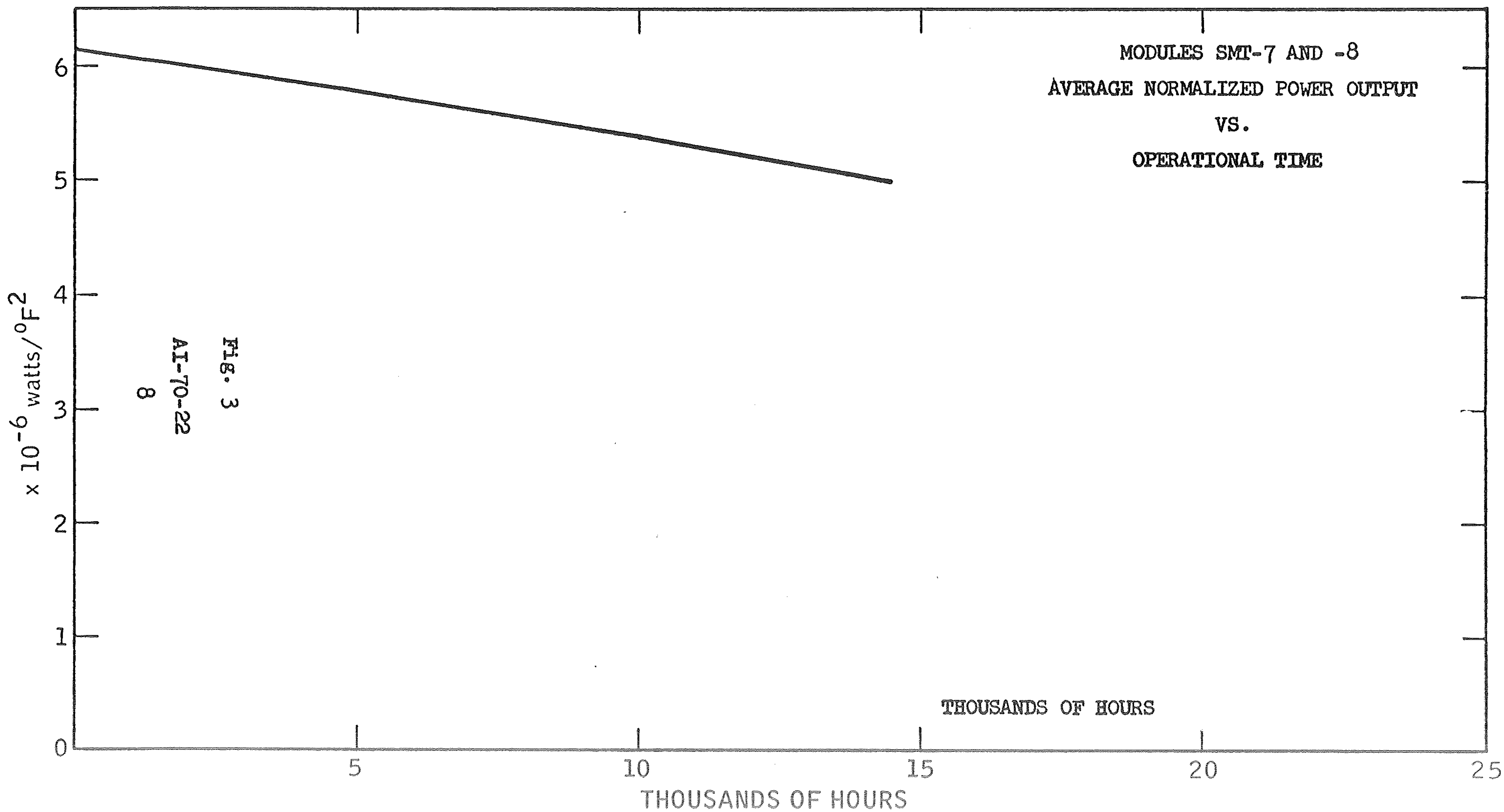
MODULES SMT-7 AND -8
AVERAGE NORMALIZED POWER OUTPUT
VS.
OPERATIONAL TIME
THOUSANDS OF HOURS
x 10-6 watts/oF2
0
1
2
3
4
5
6
5
10
15
20
25
THOUSANDS OF HOURS

Fig. 3

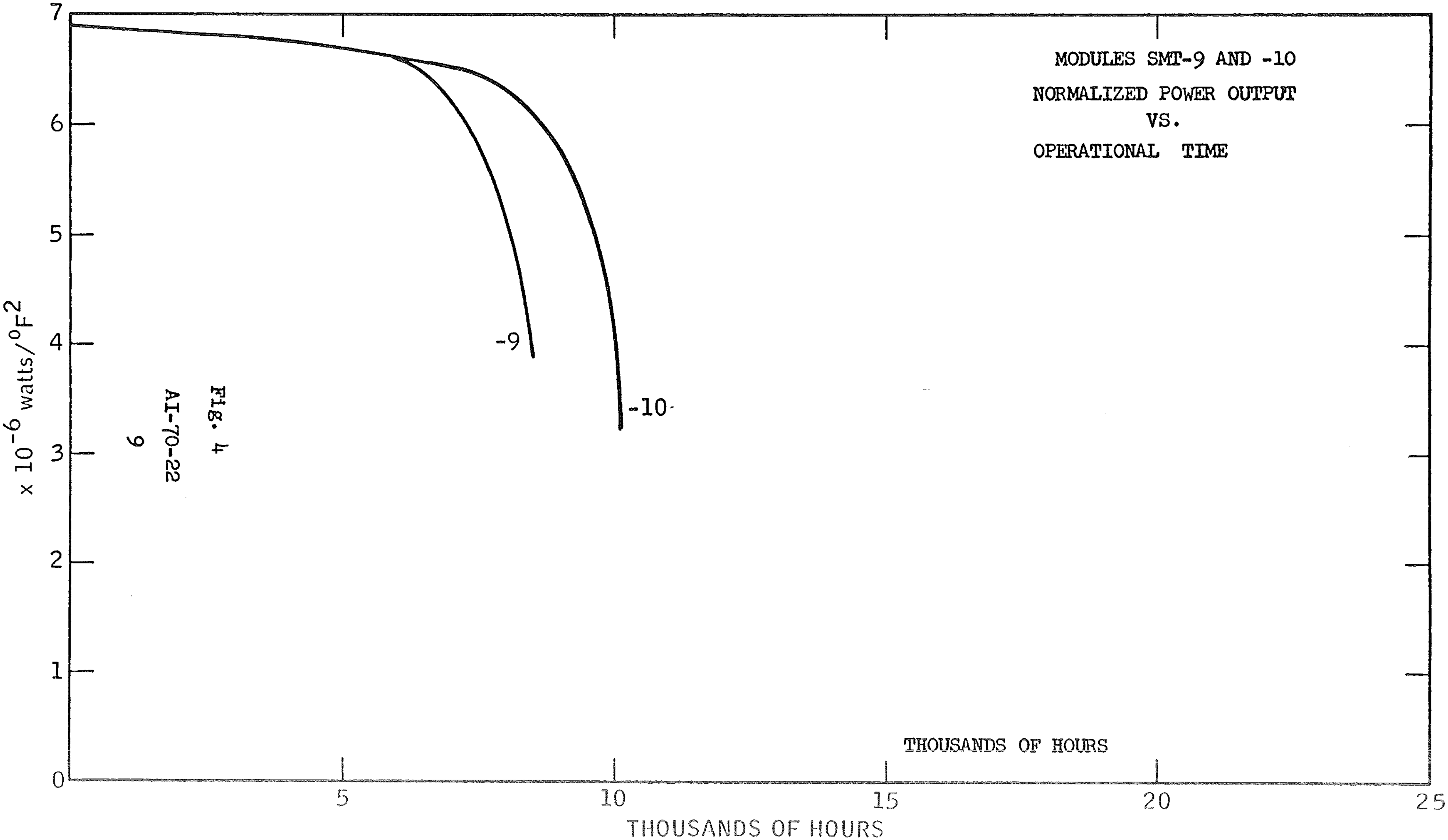
MODULES SMT-9 AND -10
NORMALIZED POWER OUTPUT
VS.
OPERATIONAL TIME
x 10^-6 watts/°F^2
THOUSANDS OF HOURS
THOUSANDS OF HOURS
-9
-10
0
1
2
3
4
5
6
7
5
10
15
20
25

Fig. 4

AI-70-22

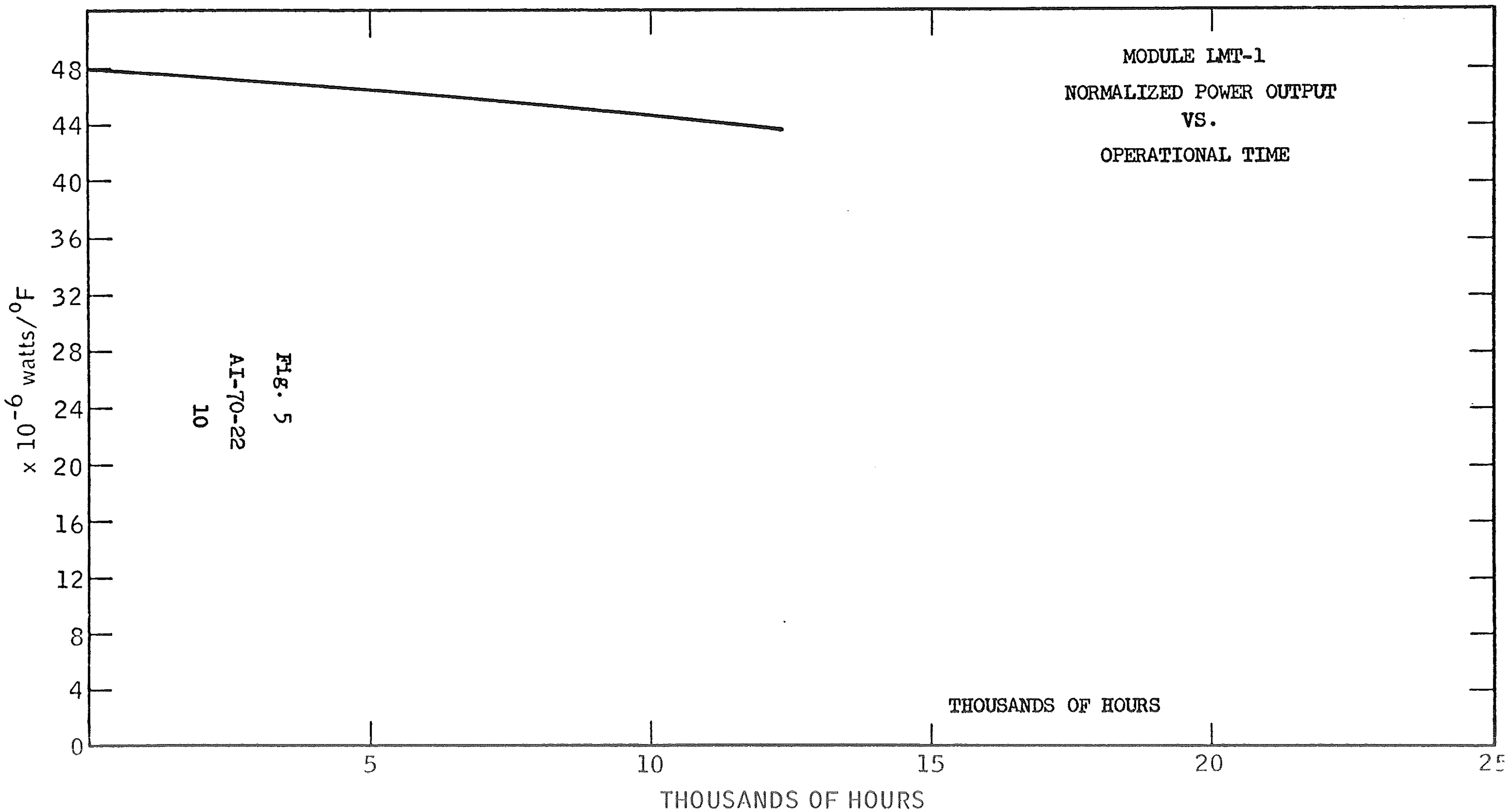
MODULE LMT-1
NORMALIZED POWER OUTPUT
VS.
OPERATIONAL TIME
THOUSANDS OF HOURS
48
44
40
36
32
28
24
20
16
12
8
4
0
5
10
15
20
25
THOUSANDS OF HOURS
x 10^{-6} watts/^oF

Fig. 5

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B. ANALYSIS OF SMT-9 AND -10 FAILURE

1. Detailed Behavior

These two modules were successors to SMT-3 and -4, which had failed at about 13,000 hours. That failure was traced definitively to reaction of tellurium and aluminum at the "P" element hot junctions. The suggested remedy was to insert a tungsten barrier at the "P" hot junctions of SMT-9 and -10. This was done.

Initial data, i.e., up to 4000 hours, on SMT-9 and -10 indicated that the solution would be successful. Even at 9227 hours, the resistance of the "P" elements had increased only 35%. However, the two "N" elements of the same couples had increased in resistance by 35 X in SMT-9, and 55% in SMT-10. At 10,109 hours, the hottest N element of SMT-10 had increased by 7.4 X in resistance. See Table I. The normalized power column, which adjusts for temperature variations, shows more clearly the steady change in the "P" elements, and the catastrophic change in the "N" elements.

TABLE I

RESISTANCE VS. TIME IN

CENTRAL COUPLES OF SMT-9 AND -10

ELEMENT	TIME (hrs.)	T_H (^oF)	RESISTANCE ($m\Omega$)	NORM. PWR. ($\times 10^{-6}$ watts/$^oF^2$)
SMT-9, N,				
CENTRAL COUPLE	140	793	3.55	1.20
	3384	807	3.42	1.21
	7030	806	4.33	0.94
	7796	801	6.76	0.59
	8544	817	19.8	0.20
	9227	832	123	0.03
SMT-9, P,				
CENTRAL COUPLE	140	797	3.14	1.25
	3384	811	3.65	1.15
	7030	805	4.13	1.11
	7796	800	4.07	1.11
	8544	815	4.34	1.07
	9227	830	4.55	1.03
SMT-10, N.				
CENTRAL COUPLE	140	798	3.56	1.20
	3384	800	3.51	1.19
	7030	796	3.66	1.11
	8544	798	4.66	0.84
	9227	778	5.53	0.71
	10109	833	26.2	0.15
SMT-10, P,				
CENTRAL COUPLE	140	796	3.18	1.25
	3384	795	3.34	1.21
	7030	790	3.87	1.13
	8544	789	3.95	1.11
	9227	770	3.98	1.10
	10109	823	4.27	1.07

It is noted that the input heat had to be continually decreased in order to counteract overtemperature, as at 8544 hours and 9227 hours, in SMT-9; also, that the temperature difference between the center couples and the end couples increased, while their cold-junction temperatures decreased.

2. Discussion

The necessary conditions to explain the observations above are:

1) The hot straps (of the center couples) remained in good thermal contact with the hot wall.

2) The thermal impedance of the elements (especially the "N" elements) increased, and/or

3) The Joulean heating in the elements increased, and/or

4) The Peltier cooling at the hot junctions decreased.

Taking these four points in order:

1) The tension-stud-and-rocker system no doubt maintained thermal contact.

2) Since the electrical impedance increased, the thermal impedance must have increased also.

3) The electrical impedance increased more than the square of the current decreased, so the product I^2R did, in fact, increase.

4) The Peltier cooling was reduced continually by the reduced electrical current.

Since these factors were all positive, tending to raise the hot-junction temperature, we need look only for an initiating process that would make one of the six elements (of a 3-couple module) become significantly higher in electrical resistance than the other five.

Any of the usual degradation processes is temperature-sensitive; therefore, the catastrophic degradation would be expected to initiate in the hottest, or center couple.

3. <u>Speculation on Causes</u>

In SMT-9 and -10, the "P" elements are contacted with tungsten, which is notably compatible with PbTe. In the predecessor SMT-3 and -4, the "P" elements faced aluminum, with which it forms a high-resistivity compound. It is reasoned, then, that in SMT-3 and -4, the degradation process almost had to start in the "P" elements; and in SMT-9 and -10, in the "N" elements.

The remaining question is why the "N" elements degraded seriously, whereas they had not (< 2%) in SMT-3 and -4. A search of fabrication and test data revealed the following pertinent differences in SMT-9 and -10.

1) A severe overtemperature (about 200°F for several hours) occurred at about 970 hours during a plant power-line switching operation; this may have caused some PbTe or Te sublimation.

2) The PKT insulating blocks were slightly shorter than in SMT-3 and -4, and the holes fitted the elements less closely.

3) The indicated "N" element hot-junction temperatures were kept generally higher, by about 15°F, than in SMT-3 and -4.

It is felt that (3) alone is of minor significance. However, one can speculate that tellurium, sublimed from the known tellurium excess in the 2P material during the accident of (1), may have migrated, in time, to the "N" elements. Tellurium is a recognized contaminant for the "N" material, causing increased resistivity. It is possible also that (2) and (3) together contributed to reduction of element cross-section by sublimation, sufficiently to initiate serious degradation. The program does not allow for a post-mortem analysis to determine actual cause.

C. GENERAL ANALYSIS OF TEST MODULE DEGRADATION

1. Observed Degradation Rates

It was reported prematurely in the "Summary" report, AI-69-16, that the operational power graphs followed a $(\text{time})^{\frac{1}{2}}$ function. The additional 15 months of test time since that report has revealed that over very long test periods, the data are fitted better by a straight line on a linear time scale, up to the point where catastrophic failure begins. This is evident in the graphs, Figures 1 - 5. Upon review of the detailed structure of the graphs shown here and in the prior reports, one can hypothesize four processes affecting the modules.

1) During the first 300 to 1000 hours, a "seating-in" improvement period.

2) During a middle period of several thousands of hours (depending on temperature), a degradation which is diffusion-controlled and follows a (time) $\frac{1}{2}$ function.

3) Next, a long period of degradation probably related to poisoning or sublimation or both, during which the rate becomes approximately linear.

4) Finally, catastrophic change related to a rapid temperature increase in the single most degraded element.

It is pointed out, with emphasis, that in a real system with nearly constant heat input and without temperature control, the process of (4) would be greatly accelerated above what has been observed in this test program A practical converter would require a safeguard against thermal "run-away" of any single element that should develop, for any reason, a significantly higher resistance than its fellows. This is a general statement not limited to the technology described herein.

2. Discussion

We would like to be able to make a valid and realistic estimate of the potential life capability of the aluminum-contacted modules.

A review has been made of all the basic design information gained from the module tests, and the best technology selected. This is summarized in outline form as follows:

a. Contacts

   (1) Aluminum

      (a) With N-type PbTe, demonstrated to be very stable at 800°F for at least 13,000 hours, at 750°F for at least 3 years.

      (b) With P-type PbTe, develops high resistance at hot-junction contacts, very temperature-dependent.

   (2) Tungsten

      (a) With P-type PbTe, demonstrated to be fairly stable at 800°F for at least 10,000 hours.

      (b) For further discussion on both "P" and "N" contacts, see paragraph below on in-house testing.

b. Straps - aluminum demonstrated to satisfactory at all temperatures as current conductor, if not attacked by Te from "P" elements.

c. Thermal Insulation

   (1) Potassium titanate (PKT) found compatible at all temperatures.

   (2) Evidence indicates that very close fit on element circumference is essential.

(3) Surrounding dimpled Al foil insulation is effective (used in LMT-1).

d. Mounting of Couples

(1) Tension-stud-and-rocker demonstrated excellent in life tests, maintaining contacts even when deteriorated.

(2) Performed well on vibration testing of 3-couple module.

e. Sublimation in High Vacuum

(1) Of PbTe-shown in SMT-3 and -4 to be negligible after 13,000 hours at 800°F, if thermal insulation (PKT) is well fitted.

(2) Of Te (excess in 2P material) - evidence not clear-- may be an ultimate cause of degradation when all other factors are corrected.

D. SUPPLEMENTARY DATA FROM OTHER PROGRAMS

Some of the reasoning and conclusions presented in Sections II.B. and IIC. above, and in II.E. below are supported by evidence obtained externally to this program. A notable instance is the STAR-2 Panel Experiment (Company-funded), built early in 1969. In this 4-couple experiment both the "N" and "P" hot junctions were tungsten-contacted, rather than only the "P" as in SMT-9 and -10. Also, the PKT blocks were fitted tightly on the elements and covered the hot junctions. After more than a year of operation at average $T_H = 812^\circ F \pm 5^\circ F$, the total resistance has increased only 6.5%; as far as can be determined, the increase is totally in the "P" elements. This evidence seems to agree with the "sublimation" postulation re failure in SMT-9 and -10. A concurrent slight increase in average Seebeck coefficient (in STAR-2) also suggests that, although the PbTe sublimation is suppressed, the excess Te may be evaporating, thus leading to reduced carrier concentration and higher material resistivity adjacent to the hot shoe.

E. EVALUATION OF TOTAL EXPERIMENTAL FINDINGS

1. Initial Performance

As reported in prior progress reports, the initial electrical performance of the aluminum-contacted PbTe couples is approximately equal to that predicted from the thermoelectric materials data, demonstrating that the total parasitic electrical loss can be made very small, certainly less than 15%, and probably less than 10%.

The conversion efficiency was shown to be 1% per $100^\circ F\ \Delta T$, "raw", in LMT-1. If the extraneous experimental losses could be eliminated, the true conversion efficiency would be 10% to 20% higher. In an optimized and well-engineered system, a conversion efficiency in the range 5% to 6% could be achieved at an average T_H of $750^\circ F$, and T_C of $300^\circ F$.

In AI-69-16, it was estimated that a specific power of at least 6 watts/lb. would be obtained in an engineered converter.

2. Integrity and Reliability

The single vibration test described in AI-69-16 is weighted heavily because of its severity (6 shakes, 3 hot and 3 cold, perpendicular axes, SNAP-10A vibration test schedule). It is believed that the tension-stud-and-rocker design can provide high mechanical integrity in an engineered converter.

In addition, this mounting appears to guarantee that an element contact, even when seriously degraded, will not separate so as to open the electrical circuit.

3. Potential Life

Table II below gives a schedule of potential life versus average hot-junction temperature. The values shown were estimated on the basis of the following assumptions:

a. The maximum hot junction temperature will be no more than 25°F above the average.

b. A limiting or protective mechanism will be incorporated to prevent or compensate for thermal "run-away" (See Section II.C.1.)

c. The best developed technology will be used, including good in-process quality control, well-fitted insulation, tungsten "P" contacts, etc.

d. The couples will not at any time be exposed to oxygen while hot.

e The end-of-life power degradation, separate from heat-source degradation, is taken to be 20%.

TABLE II

CONVERTER LIFE AND EOL EFFICIENCY VS.

AVERAGE HOT-JUNCTION TEMPERATURE

AVERAGE T_H, $^\circ F$	DEMONSTRATED LIFE	PROJECTED LIFE	* EOL EFFICIENCY
675	>> 3 years	28 yrs.	3.60%
700	>> 1.5 years	20 yrs.	3.84%
725	> 3 years	15 yrs.	4.08%
750		9 yrs.	4.32%
775	> 1.5 years	5 yrs.	4.56%

* If $\overline{T_C} = 300^\circ F$. The calculation is based on measured "raw" efficiencies, plus 20% correction, minus 20% degradation, or 0.96%/ $100^\circ F\ \Delta\ T$ (See Section II.D.1). Degradation rates are from observed values with W barriers, and adjusted by a factor of 5 X for earlier modules.

III. CONCLUSIONS

A practical thermoelectric converter can be built completely of "non-magnetic" (low permeability) materials.

The converter, if operated at temperatures of 800°F or lower, can tolerate the high vacuum of the space environment.

The thermoelectric performance, including specific power, power density, and conversion efficiency, is moderately good.

The mechanical integrity, and circuit reliability can be made excellent.

The operational stability, which is a function of temperature, is such that reasonable end-of-life efficiencies can be obtained, even for long missions.